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Momentum Profile and Final Correlation Effects of Iso-butane Inner Valence by Binary (e, 2e) Spectroscopy *

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The binding energy spectra and the momentum distributions of the valence orbitals of iso-butane, also known as methylpropane ($\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$), are studied by using a high resolution binary (e, 2e) electron momentum spectrometer, at an impact energy of 1200 eV plus the binding energy (8–32 eV) with symmetric non-coplanar kinematics. Binding energy spectra of the valence shell are obtained at a coincidence energy resolution of 0.95 eV in full width at half maximum. The experimental momentum profiles of the inner valence orbitals are obtained and compared with the theoretical momentum distributions calculated by using Hartree-Fock and density functional theory methods with the basis sets 6–31G and 6–311++G**. The pole strengths of the inner orbitals are estimated and the final correlation effects are discussed.

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Electron momentum spectroscopy (EMS) has developed rapidly since the pioneer research by Amaldi *et al.*¹ and Weigold *et al.*² Now the EMS has become a powerful experimental tool for investigating the electronic structure of atoms, molecules, biomolecules and condensed matter. It can access the complete valence shell binding energy range, though with lower energy resolution than that in most photoelectron spectroscopy (PES) studies. The binding energy can provide the information of the valence electron momentum distribution and correlation effects. In particular, EMS technique provides straight tests for quantum chemical calculations at the Hartree-Fock (HF), configuration interaction and the density function theory (DFT) levels. The details of EMS experimental techniques and the associated theoretical analysis have been reviewed in detail elsewhere.^{3–5}

Under the conditions of high impact energy and high momentum transfer, the target electron essentially undergoes a clean “knock-out” collision and the plane wave impulse approximation provides a very good description of the collision. In the binary (e, 2e) collision using symmetric non-coplanar geometry the kinematic factors are effectively constant,³ the EMS cross section for randomly oriented gas-phase targets, σ_{EMS} , could be given by,

$$\sigma_{\text{EMS}} \propto S_f^2 \int d\Omega |\langle P\Psi_f^{N-1} | \Psi_i^N \rangle|^2, \quad (1)$$

where p is the momentum of the target electron state prior to electron ejection and S_f^2 is the pole strength.⁶ Ψ_f^{N-1} and Ψ_i^N are the total electronic wavefunctions for the final ion state and the target molecule ground (initial) state, respectively. The integral represents the spherical average due to the randomly oriented gas phase target. The overlap of the ion and neutral wavefunctions in Eq. (1) is known as the Dyson orbital while the square of this quantity is referred to as the ion-neutral overlap distribution. Thus, the (e, 2e)

cross section is essentially proportional to the spherical average of the square of the Dyson orbital in the momentum space.

Equation (1) can be greatly simplified by using the Target Hartree-Fock approximation (THFA). Within the THFA, only final (ion) state correlation is allowed and the many-body wavefunctions Ψ_f^{N-1} and Ψ_i^N are approximated as independent particle determinants of ground state target Hartree-Fock orbitals in which Eq. (1) reduces to

$$\sigma_{\text{EMS}} \propto S_f^f \int d\Omega |\Psi_j(p)|^2, \quad (2)$$

where $\Psi_j(p)$ is the one-electron momentum space canonical Hartree-Fock orbital wavefunction for the j th electron, corresponding to the orbital from which the electron is ionized, S_f^f is the spectrum factor. The integral in Eq. (2) is known as the spherically averaged one-electron momentum distribution. To this extent EMS has the ability to image the electron density in “individual orbital” selected according to their binding energies.

Equation (1) has recently been re-interpreted⁷ in the context of Kohn-Sham density functional theory (DFT) and the Target Kohn-Sham approximation (TKSA) gives a result similar to Eq. (2) but with the canonical Hartree-Fock orbital replaced by a momentum space Kohn-Sham orbital $\Psi_j^{\text{KS}}(p)$,

$$\sigma_{\text{EMS}} \propto \int d\Omega |\Psi_j^{\text{KS}}(p)|^2. \quad (3)$$

It should be noted that accounting of electron correlation effects in the target ground state is included in the TKSA via the exchange correlation potential. A more detailed description of the TKSA-DFT method may be found elsewhere.⁷

Up to now, studies of the electronic structure of small-saturated hydrocarbon molecules have re-

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ceived much attention. This is because not only these molecules are prototypes of larger hydrocarbons, but also they are important species for fuels where reforming of straight chain hydrocarbons into branched chain species is of importance. Saturated hydrocarbon molecules have been widely studied by PES,^{8–11} but until recently only the methane and ethane molecules had been studied by EMS,^{12–14} due mainly to the limited coincidence energy resolution of binary (*e*, *2e*) spectrometers, which has been typically 1.2–1.5 eV full width at half maximum (FWHM) at an impact energy of 1200 eV plus the binding energy. It has only recently become possible to investigate larger hydrocarbon molecules such as propane¹⁵ and n-butane¹⁶ and this has been achieved at Tsinghua University by obtaining an EMS energy resolution of 0.95 eV FWHM with a multichannel EMS spectrometer.¹⁷ As part of a serial study of saturated hydrocarbon molecules, we now report the measurement of the complete valence shell binding energy spectra and the electron momentum profiles of iso-butane ($\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_3$) using the high energy resolution EMS spectrometer at Tsinghua University. The relatively large number of electrons in iso-butane renders accurate quantum chemical calculations quite difficult, thus the availability of good EMS experimental data is an important aid for developing satisfactory theoretical descriptions of both binding energies and the valence orbital electron densities in hydrocarbons. In particular, the inner valence region provides a very sensitive test of the many-body calculations that take the initial and final states correlation into account.

The EMS cross section σ_{EMS} of iso-butane was measured as a function of impact energy and relative azimuthal angle using an energy-dispersive multichannel electron momentum spectrometer with a symmetric non-coplanar geometry. The details of the spectrometer constructed at Tsinghua University have been reported previously.¹⁷ Two hemispherical electron energy analyzers mounted on two independent horizontal concentric turntables, each having a five element cylindrical retarding lens system, are used for selecting energetically the scattered and ejected electrons in the experiment. In the present work, the polar angles of both analyzers are fixed at 45°. One analyzer turntable is kept in a fixed position while the other is rotated by a computer controlled stepping motor to vary the relative azimuthal angle ϕ over a range of $\pm 30^\circ$. The electrons are linearly dispersed by each hemispherical analyzer along the radial direction at the exit focal plane according to their input energies. Each energy analyzer has a position sensitive detector consisting of two micro-channel plates in the double chevron configuration and a resistive anode to detect the scattered and ejected electrons in the energy dispersive exit plane. All the components of the spectrometer are in a mu-metal shielded vacuum system. A typical base pressure of the order of 10^{-7} Torr is achieved for the system. In the present experiment, the energy range of each analyzer was set at 600 ± 4 eV with a pass energy of 50 eV. Electron impact ionization was carried out at impact energy of 1200 eV plus the binding energy (8–32 eV) under a symmetric non-coplanar geometry. The energy resolution of the spectroscopy, 0.95 eV in FWHM, was measured directly by using helium as a calibration gas. The experimental momentum resolution is estimated to be better than

0.1 a.u. from a consideration of the argon *3p* angular correlation. The sample of iso-butane from Matheson (99.9% purity) was used without further purification. No evidence of impurities was found in the binding energy spectra.

The theoretical calculations of the momentum profiles in this paper were carried out, based on equations (2) and (3), by HF and DFT methods with two basis sets of 6–31 G and 6–311++G**. The keyword of the DFT calculation is B3LYP. The optimized geometry of iso-butane has been used for all calculations. In order to compare the calculated cross-sections with the experimental electron momentum profiles the effects of the finite spectrometer acceptance angles in both θ and ϕ ($\Delta\theta = \pm 0.6^\circ$ and $\Delta\phi = \pm 1.2^\circ$) were included using the Gaussian-weighted planar grid method.¹⁸

The tertiary carbon atom in iso-butane has an inequivalent *sp*³ hybrid. The point group symmetry of iso-butane is C_{3v} . According to the molecular orbital theory, the ground state electronic configuration can be written as

$$\underbrace{(1a_1)^2(1e)^4(2a_1)^2(3a_1)^2(2e)^4(4a_1)^2}_{\text{inner-valence}} \\ \underbrace{(5a_1)^2(3e)^4(4e)^4(1a_2)^2(5e)^4(6a_1)^2}_{\text{outer-valence}}$$

In the ground state, the thirty-four electrons are arranged in seventeen doubly occupied orbitals in the independent particle description. The valence electrons in iso-butane are distributed in thirteen molecular orbitals and four of the orbitals are degenerate. All the canonical molecular orbitals are either a-type or e-type. The four e-type orbitals are each double degenerate. The assignment of the order of occupation for these valence orbitals, both by PES experiments and by molecular orbital calculations, has been discussed in detail in Refs. 8–11.

To obtain the experimental momentum profiles, eleven binding energy spectra over the energy range of 8–32 eV were collected at the out-of-plane azimuthal angles $\phi = 0^\circ, 2^\circ, 4^\circ, 6^\circ, 8^\circ, 10^\circ, 12^\circ, 14^\circ, 16^\circ, 20^\circ$ and 24° in a series of sequential repetitive scans. Figure 1 shows the valence shell binding energy spectra of iso-butane in the range of 8–32 eV for measurements at $\phi = 0^\circ$ (a), $\phi = 6^\circ$ (b) and sum of all ϕ angles (c) at the impact energy of 1200 eV plus the binding energy (8–32 eV). The spectra in Fig.1 were fitted with a set of individual Gaussian peaks whose widths are combinations of the EMS instrumental energy resolution and the corresponding Franck-Condon widths derived from high resolution PES data.⁵ The fitted Gaussians for individual peaks are indicated by the dashed lines while their sum, i.e. the overall fitted spectra, are represented by the solid lines. The differences of the orbitals in FWHM are due to the vibrational broadening of the lines. The relative energy values are given by the relative ionization energies determined by high resolution PES. The differences of the relative intensities in the $\phi = 0^\circ$ and $\phi = 6^\circ$ spectra reflect the different symmetries of the valence orbitals of iso-butane molecules. The average vertical ionization potentials of the three inner orbitals of $4a_1$, $2e$, and $3a_1$ are determined to be 18.58, 21.83 and 24.83 eV by the PES data using He II radiation source.¹¹

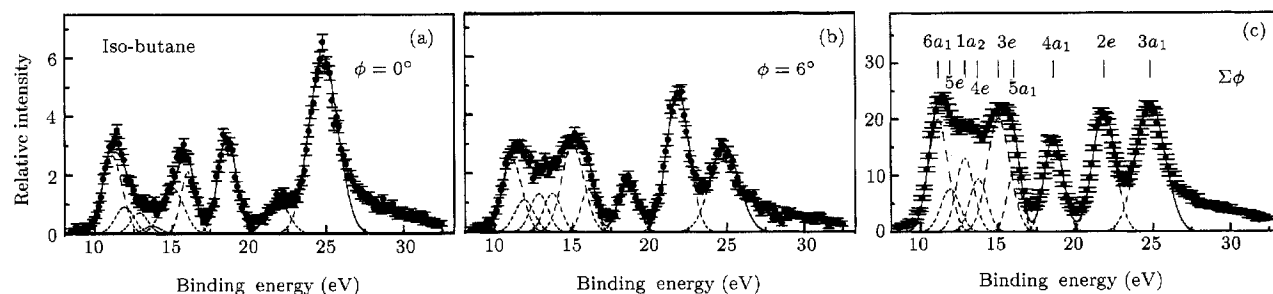


Fig. 1. Valence shell binding energy spectra at impact energy of 1200 eV plus the binding energy (8–32 eV) for iso-butane at $\phi = 0^\circ$ (a), $\phi = 6^\circ$ (b) and sum of all ϕ angles (c). The dashed lines represent the fitted Gaussians for individual peaks and the solid line for their sum, i.e. the overall fitted spectra, respectively.

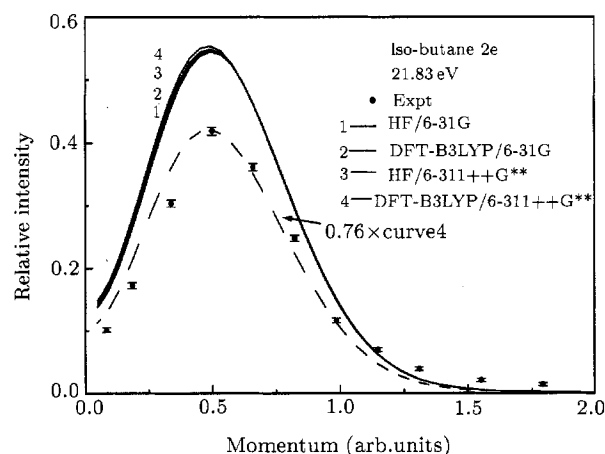


Fig. 2. Experimental and calculated momentum distributions for the inner-valence orbital $2e$ of iso-butane. The TMPs are calculated by using Hartree-Fock (curves 1 and 3) and DFT-B3LYP (curves 2 and 4) methods with the 6-31G and 6-311++G** basis sets. The segmented curve is due to the curve 4 multiplied by an estimated pole strength of 0.76.

Experimental momentum profiles (XMP's) have been extracted by deconvolution of the sequentially obtained angular-correlated binding energy spectra, and therefore the relative normalization for the different transitions is maintained. For all inner orbitals $4a_1$, $2e$, and $3a_1$, the various theoretical momentum profiles (TMP's) are obtained with the methods described above and the experimental instrumental angular resolutions have been incorporated in the calculations using the UBC RESFOLD program based on the GW-PG method.¹⁸ Experimental data and theoretical values have been rendered on a common intensity scale by normalizing the experimental to the DFT-B3LYP/6-311++G** TMP for the orbital $6a_1$ and preserving all other relative normalizations. A typical experimental momentum distributions of the inner valence orbital $2e$ is compared, in Fig. 2, with the four TMP's calculated using Hartree-Fock (curves 1 and 3) and DFT-B3LYP (curves 2 and 4) methods with the 6-31G and 6-311++G** basis sets, respectively. The comparison between the experimental data and the theoretical calculations shows that all four

calculations overestimate the experimental intensity. This indicates that some of the transition intensity from this orbital is located in the higher binding energy range due to the final state electron correlation effects. An estimated pole strength of 0.76 is used to bring the curve 4 down for shape comparison, shown by the additional segmented curve in Fig. 2. A very good shape agreement between experiment and theory is then achieved. The estimated pole strength of the orbital $3a_1$, considering the remarkable final state electron correlation effects of inner valence orbitals, is 0.6. The fact that pole strengths are notably lower than 1 for the inner orbitals confirms the existence of satellite structures, as seen in the binding energy spectra in Fig. 1, especially above 26 eV. The full details of the experimental results and the associated theoretical analysis for iso-butane will be reported later.

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